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Low Cost CE-NMR with Microcoils for Chemical Detection

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Abstract

Understanding speciation in solids and solutions is important for environmental and toxicological purposes. Capillary electrophoresis (CE) is a simple rapid separation technique that can be used to identify species in solution. CE is particularly well suited for rapid separations of metal containing samples. Direct on-capillary measurement of metal compound speciation can be obtained with nuclear magnetic resonance (NMR). The development of a low-cost microcoil CE-NMR system for in situ characterization of samples of interest is discussed. High precision laser lithography is used to produce copper sputtered microcoils that have comparable resistivity and quality factors to that of hand wound microcoils. A portable NMR system coupled with a CE system has the potential to identify chemical species in aqueous solutions. In addition, transient isotachophoresis can separate and pre-concentrate samples of interest to obtain separate chemical peaks for speciation by online NMR analysis. We are developing separation assays to determine the speciation of chemical complexes in solutions with minimal perturbation to the original sample equilibrium. On-line NMR measurements will be made downstream of the UV detector. **Copyrights** remain with the Authors.

Keywords - portable NMR, lithographic microcoils, capillary electrophoresis, CE, metal speciation, isotachophoresis

1. LLNL Laser Lithography Process and RF Microcoil Probe Development

Laser lithographic techniques are used to design and construct radio frequency (RF) copper microcoils patterned onto capillaries for portable NMR probes [1, 2]. Microcoils are developed onto the capillaries by standard lithographic techniques (see Figure 1). The capillaries are first coated with copper and photoresist layers. Then, the Laser Lithography (L-Lathe) system etches the coil pattern by ablating the photoresist down to the lower copper layer in specifically designed patterns. The copper is then electroplated into the laser etched

pattern. And finally the remaining photoresist mask and thin copper layer directly below this mask are lithographically removed leaving a precisely designed, highly reproducible copper microcoil. The L-Lathe process can produce solenoidal coils of varying OD, windings, thickness, pitch, and more complicated 3D shaped microcoil.

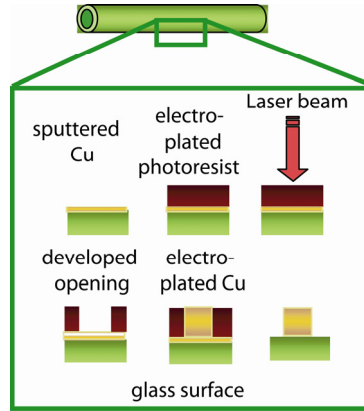


Fig 1. L-Lathe process for creating solenoidal lithographic RF copper microcoils on a capillary surface.

1.1. Microcoil Electronic Characterization

Electronic characterization of the lithographically patterned microcoils demonstrates the versatility of the production method. The resistivity of the lithographic coils ($1.85 \text{ m}\Omega\cdot\text{cm}$) is comparable to that of hand wound copper wire coils ($1.72 \text{ m}\Omega\cdot\text{cm}$) of identical size [1]. Measurements show that increasing the electroplated microcoil thickness will decrease resistance and increase the signal to noise ratio [3]. For typical solenoid RF coils, E/B_1 increases at least linearly with the sample radius. Thus, temperature rise (T_{RS}) will typically increase at least as a fourth power of coil diameter according to Equation (1).

$$T_{RS} = \frac{E^2 r_i^2}{8k} = \frac{P_s}{4hk} \quad (1)$$

Recent data [3] shows improved lithographic microcoils with lower resistivity and better quality factors than wire coils wound with a motor controlled system. Lithographic microcoils are compared in several configurations, including varying thickness, pitch, diameter, and winding number as well as compared to similar motor-wound wire coils. In addition, 2-D Ansofts Maxwell simulations of current distributions in RF coils are run on both square and round coil cross-sections; results show the solenoidal inner surface, carries the highest current loads for small OD microcoils.

2. NMR RF Microcoil Probe Design Provides Durability and Flexibility

The portable NMR probe is designed to be easily interchangeable (see Figure 2), to facilitate probe exchange for the testing of various microcoils without the need to replace the tuning circuitry each time. The RF microcoil is etched onto a capillary that removes with the interchangeable probe. The capillary and coil are jacketed in copper tubing to enhance durability and to extend the RF coil into the center of the magnetic field. Lithographic shimming coils are added to a ceramic collar surrounding the RF coil to improve magnetic field homogeneity (Figure 2). The probe and circuitry are mounted on a micrometer stage to allow for positioning of the RF microcoil in the magnetic field.

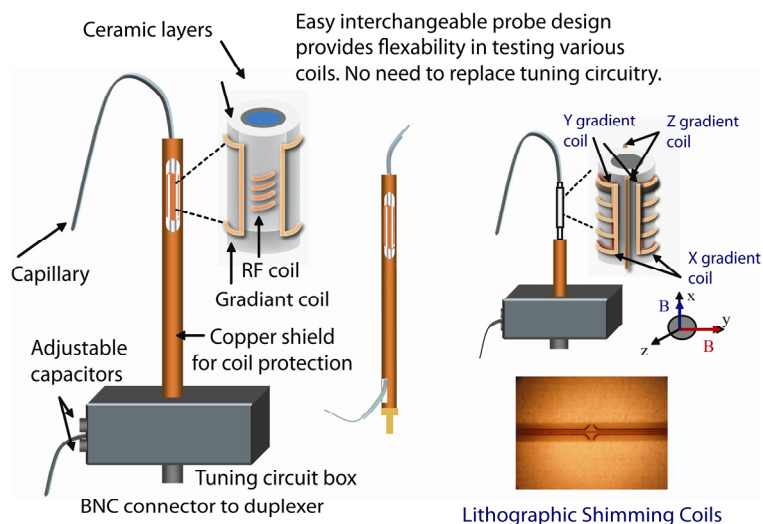


Fig 2. Portable NMR probe design showing exchangeable probe with lithographic RF microcoils and lithographic microcoil shimming design shown on outer ceramic collar.

3. Portable magnet evaluation

Several low field portable magnets have been evaluated including 1T and 2T Magnetic Solutions Halbach magnets, 1T and 1.7T Aster Enterprises box magnets, and a 0.4T Tecmag multi-ring Halbach magnet. The Magnetic Solutions Halbach magnets show best overall uniformity achieving good fits with quadratic terms (Figure 3a). The Aster magnets show a less uniform overall field (Figure 3a) but exhibit excellent shielding important for a portable system and uniform magnetic fields in the magnets' center bore. A comparison of ppm resolution for ^{19}F NMR of fluorinert in the frequency domain for high field and three low field portable Aster box magnets is shown in Figure 3b. The 1.7T Aster box magnet exhibits 1-2 ppm resolution, though signal-to-noise improvements are still desired.

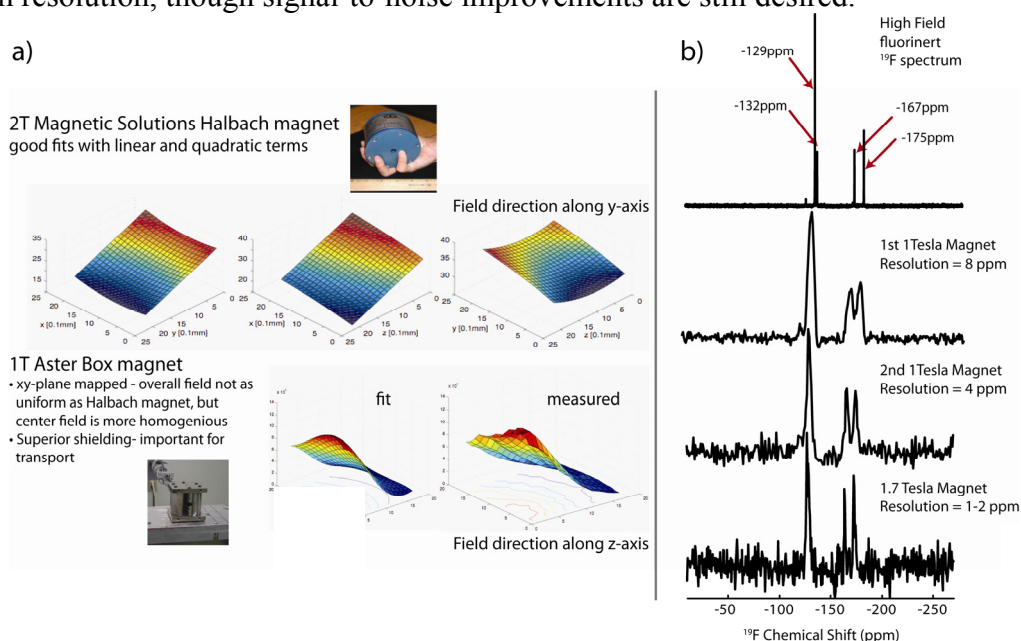


Fig 3. a) Magnetic field maps of 2T Magnetic Solutions Halbach magnet and 1T Aster Enterprises Box magnet. b) Comparison of ppm resolution using ^{19}F NMR of fluorinert in the frequency domain for high field and three low field portable Aster box magnets, two 1T and one 1.7T magnet. Data obtained with 410 μm OD, 410 μm length microcoil, and 28 scans with a 0.5 second delay time.

The portable NMR system is greatly affected by room temperature stability. Figure 4 shows temperature variations observed overnight in two environments: a) room with widely

varying temperature shifts ($\Delta T > 5^\circ\text{F}$ observed in a 10 minute interval) and b) temperature controlled room with temperature shifts less than 0.5°F during a 24 hour interval. Data was taken on the same sample repeatedly overnight with an hour delay between each 28 scan data set. Large temperature variations produce large peak shifts, Figure 4a) shows line shifts greater than 100 ppm. However, even small temperature variations shown in Figure 4b) exhibit line shifts of 9 ppm. Dilute samples requiring integration times longer than a few seconds will suffer line broadening in environments with changing temperatures. Further work is needed to negate the observed temperature drifting as the portable NMR system must function in field environments with varying conditions. Several solutions are being investigated, including adding a deuterium lock channel on top of the current shim coil geometry, adding a PID temperature controller and magnet insulation, or using magnets designed with temperature compensating materials such as SmCo.

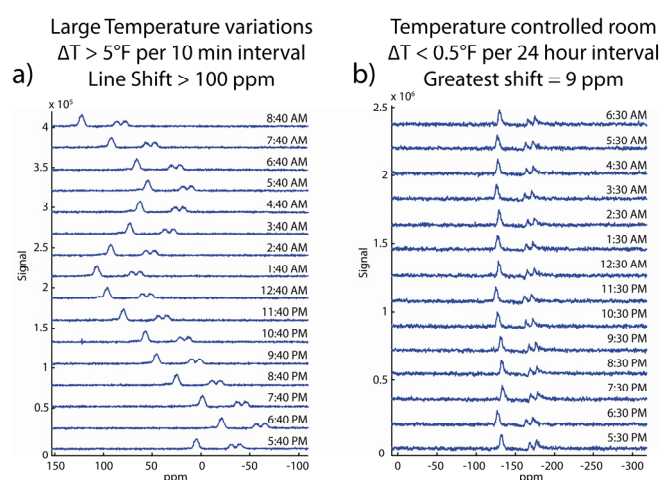


Fig 4. ^{19}F NMR of flourinert in the frequency domain taken on Aster 1.7T magnet with 28 scans and delay time of 0.5s. Data was taken overnight with a 1 hour delay between scan sets. a) data was taken in a room with temperature variations observed greater than 5°F in a 10 minute interval. b) data was taken in a room with temperature stability within 0.5°F over a 24 hour interval

Capillary electrophoresis (CE) is being investigated to provide sample pre-concentration and separation. Transient isotachophoresis [4], a CE stacking technique, can separate and pre-concentrate individual chemicals based on molecular size and charge. NMR can then provide additional speciation information by centering one of these chemical plugs in the RF microcoil. The CE will provide a specific chemical plug of interest, pre-concentrated to the online portable NMR where speciation of the chemical of interest can occur.

4. Acknowledgments

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